ATR-UV SENSOR FOR KRAFT LIQUOR MONITORING

Part I:

Simultaneous and Rapid Analysis of Hydroxide, Sulfide, and Carbonate in Kraft Liquors by Attenuated Total Reflection UV Spectroscopy

Project F035

Report 1

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

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A Progress Report

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By

J.Y. Zhu, X.S. Chai, and J. Li

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ATR-UV Sensor for Kraft Liquor Monitoring –

Part I: Simultaneous and Rapid Analysis of Hydroxide, Sulfide, and Carbonate in Kraft Liquors by Attenuated Total Reflection UV Spectroscopy

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EXECUTIVE SUMMARY

Kraft delignification rate and selectivity are strongly affected by the white liquor quality, *i.e.,* NaOH and Na_2S concentrations. The goal of kraft recovery is to produce white liquor with high concentrations of NaOH and Na_2S, and low concentrations of Na_2CO_3 and Na_2SO_4. Reliable, rapid, and accurate on-line analysis of white and green liquor compositions, mainly, the concentrations of hydroxide (or alkali), carbonate, and sulfide, can provide in-situ data to allow operators to better control the recausticizing process to produce high quality white liquor to control pulp quality and reduce pulp mill upset. Unfortunately, most pulp mills all over the world rely on a classical offline titration method, *i.e.,* ABC titration, to determine the concentration of hydroxide (or alkali), carbonate, and sulfide in white and green liquors. Because the ABC titration method can only be performed offline and takes about 30 minutes to obtain results, pulp mills only can monitor the green and white liquor composition every 2 to 4 hours and are unable to control the recausticizing operation, resulting in loss of productivity and operation upset.

The overall objective of this research is to develop a reliable and rugged on-line sensor for kraft liquor monitoring in mill recausticizing operations for process control. The capability can significantly improve mill operation, and pulp property uniformity, and reduce the possibility of evaporator fouling through better process control.

This study experimentally demonstrated Attenuated Total Reflection (ATR) UV Spectroscopy for rapid and simultaneous determination of hydroxide, sulfide, and carbonate in kraft liquors. On-line measurements were achieved using an ATR flow cell integrated with a commercial UV spectrophotometer. A multi-variant partial least-square fitting procedure was employed to develop a species concentration predictive model. The model is calibrated using a set of eighteen modified kraft liquor samples made from a mixture of a kraft mill green and white liquor (base liquor) through dilutions and additions of sodium hydroxide, sulfide, and carbonate. The concentrations of hydroxide, sulfide, and carbonate in these liquors were obtained by standard ABC titration. The ATR-UV measurements were then directly applied to one green and three white liquor samples collected from the same kraft mill. Very good agreements between ATR-UV measured and titrated concentrations of hydroxide, sulfide, and carbonate were obtained. The ATR-UV measurement is rapid and accurate and does not require sample pretreatment or dilution; therefore, it can be implemented on-line for process control in mill environments. Because of the low cost and ease in maintenance, the ATR-UV technique may provide a better alternative to ATR-NIR or -FTIR methods.

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INTRODUCTION

One of the main objectives of the chemical recovery cycle in a kraft pulp mill is to regenerate sodium hydroxide to remake pulping chemicals. A modern chemical recovery process can recover about 95% of sodium hydroxide for pulp production. Because kraft delignification rate and selectivity are strongly affected by the white liquor quality, i.e., NaOH and Na_2S concentrations, the goal of kraft recovery is to produce white liquor with high concentrations of NaOH and Na_2S, and low concentrations of Na_2CO_3 and Na_2SO_4. Reliable, rapid, and accurate on-line complete analysis of white and green liquor compositions, mainly, the concentrations of hydroxide (or alkali), carbonate, and sulfide, can provide in-situ data to allow operators to better control the recausticizing process to produce high quality white liquor to control pulp quality and reduce operation dead load. Unfortunately, most pulp mills all over the world rely on a classical offline titration method, i.e., ABC titration [1], to determine the concentration of hydroxide (or alkali), carbonate, and sulfide in white and green liquors. Because the ABC titration method can only be performed offline and takes about 30 minutes to obtain results, pulp mills can only monitor the green and white liquor composition every 2 to 4 hours and are unable to control the recausticizing operation, resulting in the loss of productivity and high energy cost due to unnecessary dead load and low recausticizing efficiency.

Due to the high maintenance requirements, the on-line and off-line automatic titrators have not been widely accepted in mill applications. Development of non-titration based sensors for rapid kraft liquor analysis has attracted great interest. Conductivity [2-4] sensors and conventional ultra-violet (UV) spectroscopy [5] have been developed. However, these sensors can only provide single component measurements, i.e., the conductivity can only monitor hydroxide and UV spectroscopy [5] has to be used with other techniques for multi-component analysis. Furthermore, sample dilution by a factor of 1000 is required in using the conventional UV technique [5] to detect the absorption of sulfide in white and green liquors due to saturation. A high dilution ratio not only compromises the measurement accuracy but also makes sulfide determination impossible unless a high degree of dissolved oxygen removal in the water used for dilution is achieved. Because the sulfide in diluted solution can be easily oxidized by the dissolved oxygen in the water (the equilibrium concentration of the dissolved oxygen at room temperature in water is at the

same order of magnitude as the sulfide concentration). Recently, near-infrared (NIR) spectroscopy [6, 7] has been developed for simultaneous analysis of alkali, sulfide, and carbonate in white and green liquors. Because, there are no identifiable absorption peaks or bands corresponding to the species of interest in the kraft liquors, i.e., sulfide, hydroxide, and carbonate, in the NIR absorption spectra, together with the spectral interference from the absorption of water in the entire NIR range, the measurement accuracy of the NIR technique [6,7] is severally compromised when using a multivariate partial least square analysis to derive species concentrations from the overall shape of the recorded spectra.

Attenuated total reflection (ATR) or internal reflection spectroscopy was developed in the 60s by Fahrenfort [8] and Harrick [9] based on Newton's discovery that an evanescent wave extends in the rarer medium beyond the interface between two media of different refractive indices. One key characteristic of the ATR spectroscopy is that the optical path length of each pass of the evanescent wave is very short on the order of 1-2 micrometers, which makes it particularly applicable to analysis of very concentrated samples without dilution. Because most species of interest in the kraft liquor absorbs in the IR or UV range, using ATR-IR or ATR-UV spectroscopy can provide the interaction of a IR or UV evanescent wave with the absorption species in the liquor in a very short optical path length to produce a unsaturated signal for species concentration determination. Leclerc and Hogikyan [10] applied ATR-IR to measure effective alkali, carbonate, sulfate, and thiosulfate concentration in kraft liquors. Unfortunately, the ATR-IR technique is not capable of providing the sulfide concentration, a very important parameter for process control in kraft reacusticizing operations.

ATR-UV technique [11] has the advantages of low cost and easy maintenance of the UV spectroscopy for kraft liquor analysis. One of the present authors Chai [12] demonstrated the feasibility of analyzing NaOH and Na_2S concentrations simultaneously in a synthetic white liquor by ATR at the UV-Vis range in 1994. Later, Chai et al. [13] successfully performed in-line simultaneous monitoring of sulfide and polysulfide in a lab-scale electrochemical production of polysulfide from a synthetic kraft white liquor. However, the synthetic white liquors that Chai [12, 13] used did not contain carbonate. In this study, we will demonstrate the feasibility of using the ATR-UV technique for

simultaneous determination of hydroxide, sulfide, and carbonate in kraft white and green liquors.

PRINCIPLE AND METHODOLOGY

ATR Principle

Figure 1 shows the schematic of the measuring principle of an ATR-probe. A detailed description of the ATR principle can be found in the book by Harrick [9]. A transparent probe of high refractive index (n_p) is brought into contact with a sample that must have a lower refractive index (n_s). Light is introduced to the probe at an incident angle, θ, toward the interface between the probe boundary and the sample. If the angle of incidence, θ, is greater than the critical angle θ_c (given by Snell's law: $sin\theta_c = n_s / n_p$), total reflection will occur when the light hits the probe boundary. At each reflection point, the light will extend into the medium (sample) in the form of an evanescent wave [8, 9] and is absorbed by the sample. Therefore, the light reflected back to the probe carries the spectral information about the physical properties of the sample and can be recorded by a spectrometer.

The transmittance of ATR absorption spectroscopy follows Beer's law

$$T = \frac{I}{I_0} = \exp(-\varepsilon \cdot C \cdot b_{eff}) = \exp(-a) \qquad (1)$$

where T is transmittance through one reflection, I and I_0 are the spectral intensity of a sample and the reference, respectively, ε is the absorption coefficient, C is the molar concentration of the substance to be analyzed, b_{eff} is the effective absorption path length of a single pass, and a is the absorbance of one pass.

Unlike the conventional absorption spectroscopy, the effective path length, b_{eff}, in ATR spectroscopy is a function of many parameters, such as wavelength, refractive indices of probe material and the sample medium, the angle of incidence, and the state of polarization of the incident light, according to Schlemmer and Katzer [11]. The refractive index of the sample medium is the dominant factor that contributes to the effective path. Because the refractive index of the sample medium not only depends on the sample temperature and the concentration of the absorbing substances, but also on the concentration

of the nonabsorbing substances, the ATR signal also contains information about the nonabsorbing substances that can be used to determine the concentration of nonabsorbing species, a unique characteristic of ATR spectroscopy.

Neglecting the reflection loss, the transmittance of an ATR probe with z reflections can be expressed as:

$$T^z = [\exp(-a)]^z = \exp(-za) = \exp(-z \cdot \varepsilon \cdot C \cdot b_{eff}) \qquad (2)$$

The optical path length per reflection, b_{eff}, is about 1-2 μm. One can change the number of reflections and thus the sensitivity of an ATR system by varying the length of the ATR probe.

Following the definition of absorbance in conventional absorption spectroscopy, we can express absorbance in ATR spectroscopy with z reflections as,

$$a_{ATR}^z = -\ln T^z = za = z \cdot \varepsilon \cdot C \cdot b_{eff} \qquad (3)$$

Equation (3) indicate that the absorbance in ATR spectroscopy is linearly proportional to the molar concentration, C, of the species to be analyzed even when a multi-pass ATR probe is used. However, the effective absorption path length b_{eff} is not a constant as we discussed in the previous section, rather depends on the liquor refraction index that is a function of the liquor composition, which makes linear calibration not possible. Mathematically, we can represent the measured ATR absorption spectral intensity, A, at a given wavelength λ in a multi-component liquor as,

$$A_\lambda = k \cdot z\left[(\varepsilon_1 C_1 + \varepsilon_2 C_2 + ... + \varepsilon_n C_n) \cdot b_{eff}(C_1, C_2, ...C_n, \lambda, \theta, n_p, \perp, \parallel)\right] \qquad (4)$$

where k is the instrument response function (including the responses of the detectors, spectrometer slit, and optical components, etc.) of the ATR system, ε_i and C_i are the absorption coefficient and molar concentration of species i in the liquor, respectively. λ is wavelength of interest. θ is the incident angle of the light into the ATR probe. n_p is the refractive index of the ATR probe material. $\perp$ and $\parallel$ are the state of polarization of the light source. For a given ATR spectroscopy system, the light incident angle, the probe material, and the state of polarization of the light source are fixed, we can simplify Eqn. (4) as follow,

$$A_\lambda = k \cdot z\left[(\varepsilon_1 C_1 + \varepsilon_2 C_2 + ... + \varepsilon_n C_n) \cdot b_{eff}(C_1, C_2, ... C_n, \lambda)\right] \quad (5)$$

Calibration

Eqn. (5) clearly indicate that conventional linear calibration technique cannot be used in ATR spectroscopy in theory even though absorption peaks or bands of the species of interest can be clearly identified in the recorded spectra. Chemometrics [14, 15] is developed for solving complex calibration problems in process analytical chemistry. Multivariate partial least square (MPLS) [16-18] analysis is one of the most frequently used technique in chemometrics. In this study a MPLS procedure is used for calibration and prediction of ATR measurements.

MPLS is a mathematical algorithm for solving complex multivariable linear relationships. MPLS adopted nonlinear modifications [19, 20] to solve nonlinear physical problems, such as the one shown in Eqn. (5). The detailed description of the MPLS algorithm is rather complicated and can be found in the tutorial by Geladi and Kowalski [16] and in other literature [17-20]. For simplicity in explaining the basic concept of MPLS, a linear physical problem is used in the following discussion. The n independent variables, i.e., the species concentrations, C_i, and the dependent variables, i.e., the absorption spectral intensity at a specific wavelength, A_λ, have a linear relationship,

$$A_\lambda = \sum_n C_i k_i + e \quad (6)$$

Calibration of the physical problem requires a set of samples, m, of known species concentration C_i. Spectroscopy measurements were conducted to give absorptions, or spectral intensities, at a set of wavelengths, j. The calibration information is arranged to form a matrix expression:

$$\mathbf{A} = \mathbf{CK} + \mathbf{E} \quad (7)$$

Where the matrix **A** with a size of mxj is called the descriptive spectral data block, matrix **C** with a size of mxn is the independent variable block, matrix **K** with a size of nxj is the calibration coefficient matrix, and **E** is the residual matrix. In obtaining matrix equation (7), the spectral intensities at all the wavelengths measured from the same sample were put in the same row. For a total of m samples, there are m rows. For a total of j wavelengths scanned, there are j columns in each row. Because there are total n species to be

determined, matrix **C** has n columns. To get unique solution, the number of calibration samples has to be greater than or equal to the number of unknown species to be determined, i.e., $m \geq n$. Once the calibration data are presented in the form of matrix equation (7), MPLS then builds an outer relation for the independent variable block **X** by expressing **X** into a full rank matrix of rank r,

$$\mathbf{C} = \mathbf{T}\mathbf{P}^{\mathrm{T}} + \mathbf{E} = \sum_{r} t_i p_i^T + \mathbf{E} \tag{8}$$

The MPLS also builds another outer relation for the descriptive data **Y** block in the same way,

$$\mathbf{A} = \mathbf{U}\mathbf{Q}^{\mathrm{T}} + \mathbf{F} = \sum_{r} u_i q_i^T + \mathbf{F} \tag{9}$$

The matrices **T** and **U** are called scores and the **P** and **Q** are called loadings. $\mathbf{P}^{\mathrm{T}}$ and $\mathbf{Q}^{\mathrm{T}}$ are the transpose matrices of **P** and **Q**. The most critical relation in MPLS is the inner relation that relates Matrix Eqn. (8) and (9) as follow,

$$\mathbf{U} = \mathbf{K}\mathbf{T} \tag{10}$$

Nonlinear iterative partial least square (NIPALS) technique is often used to find the inner relationship (Eqn. (10)) between the components of the independent block **C** and the descriptive data block **A**. Selection the number of latent variables in the inner relationship is important. For a nonlinear physical problem as described in eqn. (5), the numbers of latent variables is often greater than the numbers of independent variables, n, to account for the nonlinerities. Once the inner relationship is obtained through the NIPALS algorithm, species concentration prediction can be made from the set of measured descriptive spectral intensities using MPLS.

In summary, the calibration process in MPLS is to seek the inner relationship (model) between the known independent variable data block **C** and the measured (known) description spectral intensity data block **A**. Once the calibration relationship (model) is established, prediction of species concentration C_i can be made from any given set of measured spectral intensity data A_j. Commercial software now is available to conduct this very complicated MPLS analysis.

There are three independent variables, sulfide, alkali, and carbonate, or n =3, to be determined in the present study. Kraft liquors contain many minor unknown species, such as thiosulfate, chloride, sulfate, etc. To reduce the effects of the minor species through affecting refraction index and spectral contribution, we used a base liquor to make the calibration liquor samples. The base liquor is made of a mill white liquor and of a mill green liquor collected from a kraft mill. The sulfide, alkali, and carbonate concentrations in the white and green liquor were first obtained by ABC titration. We then made 14 calibration samples, m = 14, by adding various amounts of hydroxide, sulfide, and carbonate into the base liquor. The concentrations of alkali, sulfide, and carbonate in the calibration samples, therefore, are known. During spectral data collection, we obtained 71 spectral intensities, j = 71, in a wavelength range between 190 – 260 nm to obtain the calibration model using the MPLS algorithm.

In view of the complicated calibration procedure using MPLS, we would like to point out that under most normal kraft mill operations, the liquor composition does not vary significantly, therefore the effect of liquor composition on the refractive index of the liquor can be treated as a constant and the effective optical path length of the ATR system is fairly constant. Then Eqn. (5) reduces to a linear equation, with clearly identifiable absorption bands of sulfide, hydroxide, and carbonate in ATR-UV spectroscopy, linear calibration can be applied as we demonstrated in our mill trial studies [21, 22], a significant advantage of ATR-UV over the NIR technique [6, 7] for kraft liquor analysis in recausticizing operations.

EEPERIMENTAL

Apparatus

All measurements were conducted in a laboratory ATR-UV system. The system consists of an ATR-UV flow cell with one path (reflection) (Axion, model TNL-120H23-3, CA, USA) for on-line analysis, a peristaltic pump (RP-1, Rainin, Emeryville, CA, USA), a 25-mL beaker, tubing and connectors, and an UV/Vis spectrophotometer (UV-8452, Hewlett-Packard, now Agilent Technologies, CA, USA.). The ATR cell consists of an ATR probe made of a quartz rod and a housing unit. Figure 2 shows a schematic diagram of the ATR-UV system. Kraft white or green liquor is circulated through the ATR cell by the peristaltic pump. The ATR cell is placed at the flow cell position of the spectrophotometer

for continuous absorption measurements over the entire UV/Vis range by the spectrophotometer equipped with an HP ChemStation for real-time spectral data collection.

Chemicals and Materials

Analytical grade sodium hydroxide, sodium sulfide, and sodium carbonate from commercial sources were used to make aqueous solutions of NaOH, Na_2S, and Na_2CO_3. Actual kraft white and green liquors obtained from a kraft pulp mill were also used for calibration and demonstration.

RESULTS AND DISCUSSIONS

ATR-UV Measurements in Aqueous Solutions of Hydroxide, Sulfide, and Carbonate

To demonstrate the ATR spectral response of hydroxide, sulfide, and carbonate in the UV range, we obtained absorption spectra of aqueous solutions of hydroxide, sulfide, and carbonate with concentrations of 2, 1, and 1 mole/L, respectively, using the present ATR flow cell. As shown in Fig. 3, the ATR spectra of these three species indicate that hydroxide and carbonate absorb in the range of 190 to 210 nm, while sulfide absorption showed a broad peak at 230 nm and high absorbance below 210 nm as well. This is because when sodium sulfide is dissolved in water, it forms both hydrogen sulfide and hydroxide ions [23], that is,

$$S^{2-} + H_2O \Rightarrow HS^- + OH^-$$

Therefore, the two species, hydrogen sulfide (HS^-) and hydroxide (OH^-) ions, contribute to the spectrum of sodium sulfide solution. The absorption at wavelength around 195 nm is from OH^- ions, and the absorption peak exhibited at 230 nm is due to HS^- ions. Figure 3 also shows that the absorption of hydroxide is much higher than that of carbonate.

Chai et al. [12, 13] were not able to obtain an ATR spectral response at a low UV wavelength range (below 210 nm) due to the technical limitation of their instrument. Therefore, very important spectra information about the absorption of hydroxide and carbonate was not obtained. Hydroxide was categorized as a nonabsorbing substance in their studies. Therefore, hydroxide prediction must rely on sulfide absorption in the range of 210 to 260 nm, with spectral contribution from the changing of the solution refractive

index, due to the presence of the nonabsorbing substances ion the solution, i.e., hydroxide. As mentioned previously, the synthetic white liquors that Chai et al. [12, 13] used did not contain carbonate. The prediction of carbonate was not attempted in their studies [12, 13]. When the spectral contribution from the nonabsorbing substances presented in the aqueous solution of an absorbing analyte is not significant, the prediction of the concentrations of the nonabsorbing substances by MPSL chemometric analysis will be inaccurate. In the present study, we extended the ATR-UV spectral range to 190 nm and found the absorption spectra of hydroxide and carbonate; therefore, these two substances will no longer be treated as nonabsorbing species. By using the spectral fingerprints of hydroxide and carbonate in ATR-UV spectroscopy, we can significantly improve the reliability in the analysis of kraft liquors.

ATR-UV Measurements in Kraft Mill White and Green Liquors

Figure 4 shows the spectra of white and green liquor samples from a kraft mill. These liquors consist of three major components, i.e., sulfide, hydroxide, and carbonate. Only HS^- ions contribute to the absorption at wavelengths around 230 nm, and the absorption of hydroxide and carbonate mainly contribute at the wavelengths blow 210 nm. The concentrations of HS^- ions in these two liquors are quite close as shown in Fig. 4. In the green liquor, the concentration of carbonate is very high, while the hydroxide is the dominant species in the white liquor. Because the absorptivity of hydroxide is very high, the absorption of the white liquor is much higher than that of the green liquor below 210 nm.

Effect of Minor Species on the Measurements

There are several minor species in kraft white and green liquors, such as thiosulfate, sulfate, and chloride. The presence of these species alters the ATR-UV absorption spectrum through direct absorption (especially for thiosulfate in the lower UV wavelength) in the UV region and contribution to the refractive index of the liquor. Significant errors may result in the prediction of kraft mill samples if the calibration database is obtained using the synthetic solutions from pure aqueous solutions of hydroxide, sulfide, and carbonate. To obtain good predictive accuracy, it is suggested that mill liquors from the same source (mill) should be used to make the calibration samples in calibration experiments.

Temperature Effect

The effect of temperature on ATR-UV spectrum was investigated by Chai et al. [13]. It was found that the absorption peak for sulfide was shifted about 5 nm toward the visible region at a temperature of 90°C compared to results obtained at room temperature of 25°C. Furthermore, the absorption peak intensity decreased about 17 % over a temperature range of 20 to 90°C. This temperature effect is not sample specific. Chai et al. [13] found that a change of temperature of about ± 5°C only produces a 2% error in absorption. In this study, we confirmed that ATR absorption intensity decreases linearly with the increase of temperature. However, if relatively good temperature control of the testing liquor, e.g., ± 2°C, is obtained before the liquor enters the flow cell, it is not necessary to include temperature as a parameter in calibration to ensure the accuracy of the analysis. All measurements were conducted at room temperature in this study.

The Effect of Corrosion of the ATR Probe

Quartz is the only possible material to choose for UV spectroscopy applications. Theoretically, hydroxide can attack quartz, which could affect measurements. We conducted a corrosion test by submerging a similar quartz rod in a 10 mol/L NaOH solution for about one month. Visual inspection using SEM shows that the corrosion on the surface of the quartz is negligible. Furthermore, we did not find any spectra distortion after many hours (>1000 hours) of measurements using the present ATR probe, indicating that corrosion is negligible with proper water flush after each experiment.

Application

To demonstrate the capability of ATR-UV spectroscopy for kraft liquor analysis, we applied the present ATR-UV system to measure one green liquor and three white liquors collected from a kraft pulp mill. The green liquor was sampled after the clarification. The three white liquors were sampled in the first retention tank (WL-1), at the discharge of the 3rd retention tank (WL-2), and at the slaker discharge (WL-3), respectively. A set of eighteen solutions was made using various combinations of the green and the first white liquor sample (WL-1) with addition of various amounts of hydroxide, sulfide, and carbonate for calibration and validation. The final concentration range of the eighteen liquors was very broad to cover all the possible concentrations of green and white liquors in the mill that

provided us with the samples. The concentrations of hydroxide, sulfide, and carbonate in these eighteen solutions were titrated by the ABC standard method [1]. The titrated values of the fourteen solutions were used for calibration to determine the parameters for the predictive model using MPLS analysis discussed previously. We reserved four solutions that were not used in calibration to conduct the first step validation of the predictive model. Figures 5 to 7 show the comparison between the titrated and model predicted concentrations of hydroxide, sulfide, and carbonate in the fourteen solutions for calibration (open symbols) and the four solutions for validation (solid symbols). The results shown in the figures also indicate that predicted concentrations in the four reserved solutions were validated by the titration results.

After the first-step validation using the four reserved solutions, we then measured the hydroxide, sulfide, and carbonate concentrations of the green and white liquors from the kraft mill using the same calibrated predictive model described in above. We also conducted ABC titration for these four kraft mill liquors. Table 1 shows the ATR-UV measurements along with ABC titrated values of the hydroxide, sulfide, and carbonate concentrations in these four liquor samples. Very good agreements were obtained between the ATR-UV measurements and the titration results, in particular, for hydroxide and sulfide. The maximum relative standard deviations in hydroxide and sulfide measurements in these four liquors are less than 5 and 2%, respectively. The relatively large errors (about 10%) in carbonate measurements are mainly due to the low absorptivities of carbonate in UV range. One can expect that a relatively large error may result in carbonate measurements in white liquors in which the carbonate concentration is relatively low.

CONCLUSIONS

This study demonstrated the principles and applicability of ATR-UV spectroscopy for simultaneous analysis of sodium hydroxide, sulfide, and carbonate concentrations in kraft white and green liquors. The ATR-UV spectra of kraft liquors can be analyzed and solved for the concentration of sulfide, hydroxide and carbonate using a calibration model based on amulti-variant partial-least-squares fitting procedure. Very good agreement between ATR-UV measured and titrated concentrations of hydroxide, sulfide, and carbonate was obtained. The ATR-UV measurement is rapid and accurate, and does not require

sample pretreatment or dilution; therefore, it can be used to develop on-line or in-line sensors for kraft process monitoring in mill environments.

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List of Figures

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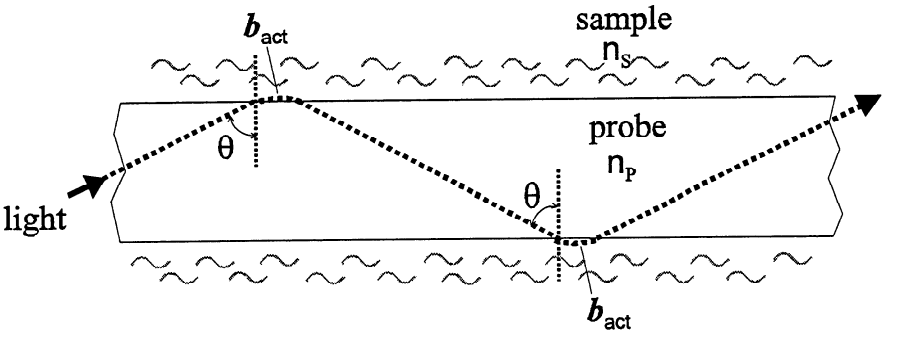

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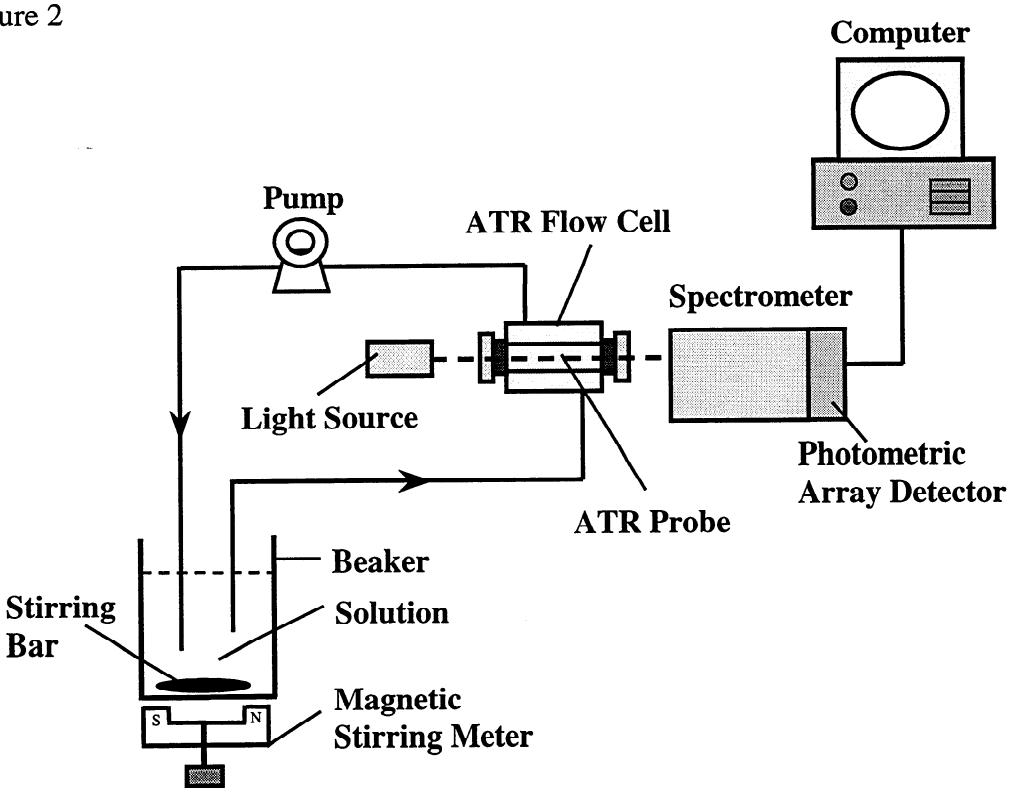

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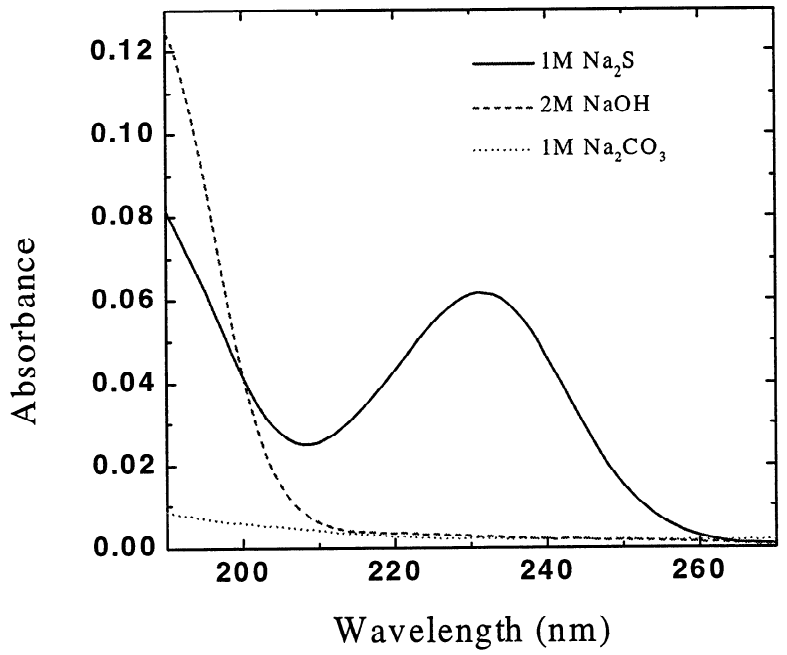

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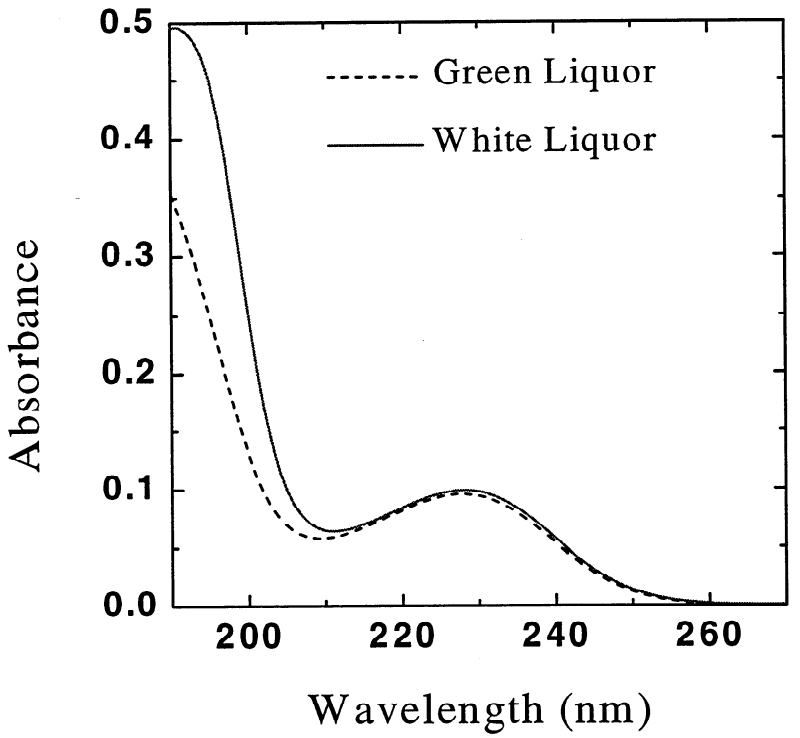

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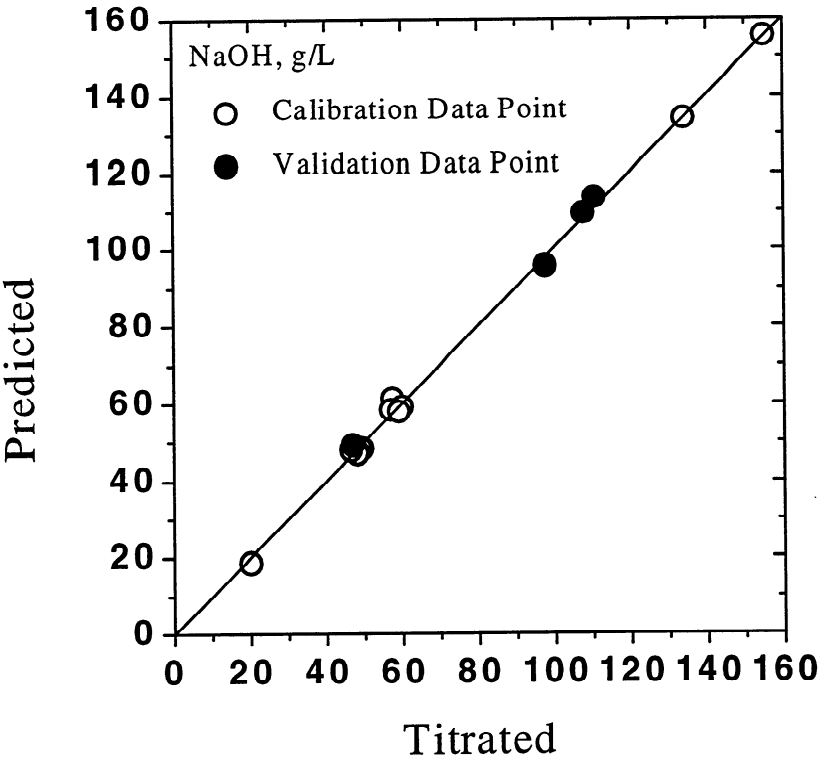

Figure 6

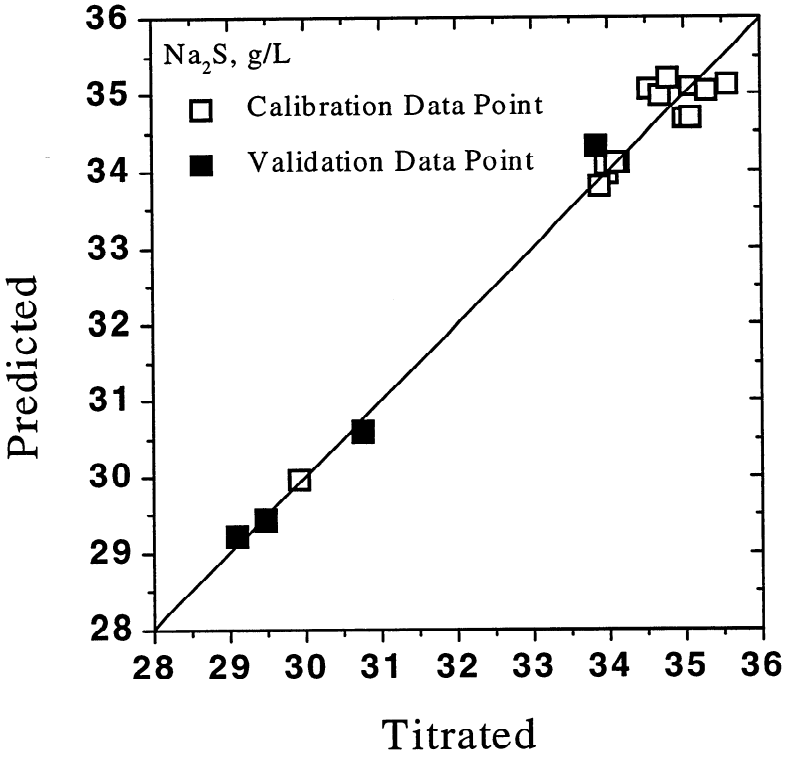

Figure 7

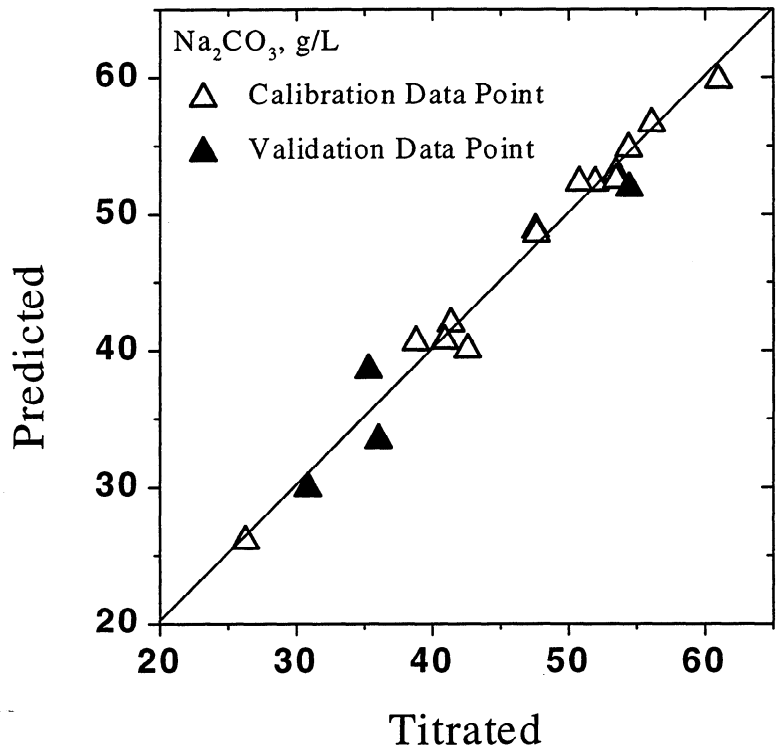

Table I. Comparisons between ATR measurements and titrated concentrations of hydroxide, sulfide, and carbonate in four kraft mill liquors

Sample*	NaOH, g/L			Na_2S, g/L			Na_2CO_3		
	Titra.	ATR	RSD,%	Titra.	ATR	RSD,%	Titra.	ATR	RSD,%
GL	47.2	48.9	3.8	33.9	34.3	1.3	54.4	51.9	-4.7
WL-1	107.6	109.3	1.5	29.1	29.2	0.4	36.0	33.4	-7.2
WL-2	110.9	113.4	2.2	29.5	29.4	-0.1	30.8	29.9	-2.8
WL-3	97.9	95.6	-2.4	30.8	30.6	-0.6	35.3	38.6	9.3

* GL: green liquor. WL: white liquor.